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Chemical stabilization of soil organic nitrogen by phenolic lignin residues in anaerobic agroecosystems

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Abstract

This review summarizes independent reports of yield decreases in several agricultural systems that are associated with repeated cropping under wet or submerged soil conditions. Crop and soil data from most of these agroecosystems have led researchers to attribute yield decreases to a reduction in crop uptake of N mineralized from soil organic matter (SOM). These trends are most evident in several long-term field experiments on continuous lowland rice systems in the Philippines, but similar trends are evident in a continuous rice rotation in Arkansas, USA and with no-till cropping systems in North American regions with cool, wet climatic conditions in Spring. Soil analyses from some of these systems have found an accumulation of phenolic lignin compounds in SOM. Phenolic compounds covalently bind nitrogenous compounds into recalcitrant forms in laboratory conditions and occurrence of this chemical immobilization under field conditions would be consistent with field observations of reduced soil N supply. However, technological shortcomings have precluded its demonstration for naturally formed SOM. Through recent advances in nuclear magnetic resonance spectroscopy, agronomically significant quantities of lignin-bound N were found in a triple-cropped rice soil in the Philippines. A major research challenge is to demonstrate in the anaerobic agroecosystems that these lignin residues bind sufficient quantities of soil N to cause the observed yield decreases. A key objective will be to elucidate the cycling dynamics of lignin-bound N relative to the seasonal pattern of crop N demand. Anaerobic decomposition of crop residues may be the key feature of anaerobic cropping systems that promotes the accumulation of phenolic lignin residues and hence the covalent binding of soil N. Potential mitigation options include improved timing of applied N fertilizer, which has already been shown to reverse yield decreases in tropical rice, and aerobic decomposition of crop residues, which can be accomplished through field drainage or timing of tillage operations. Future research will evaluate whether aerobic decomposition promotes the formation of phenol-depleted SOM and greater in-season N mineralization, even when the soil is otherwise maintained under flooded conditions during the growing season.

Keywords: Anaerobic; Lignin; Nitrogen; NMR; Soil organic matter; Phenols; Rice

1. Introduction

Soil organic matter (SOM) contains the vast majority of C, N, P and S that are found in soil. Its chemical nature is thought to influence the storage and release of these essential nutrients into plant-available forms. Yet evidence for such an influence is sparse, largely due to the inability to determine the exact chemical nature of SOM (MacCarthy, 2001) or even the bonding environments of SOM-bound nutrients. Recent studies have identified the accumulation of phenolic compounds in the SOM of submerged soils that were intensively cropped to irrigated lowland rice (*Oryza sativa* L.) in the Philippines (Olk et al., 1996, 1998). Using newly developed analytical techniques to identify the bonding environments of C with N, phenolic lignin residues were shown to have bound covalently with N in a humic acid fraction (Schmidt-Rohr et al., 2004). The

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resulting chemical stabilization was hypothesized to have contributed to an observed long-term decrease in availability of soil N and an associated decline in rice grain yield. In this review we summarize the concepts gained from this study of continuous cultivation to irrigated lowland rice, and we report independent observations from other agroecosystems in which soil remains anaerobic or partly anaerobic during the year and for which soil data suggest the covalent binding of soil N by lignin residues.

2. Intensive lowland rice cropping in tropical Asia

2.1. Yield trends and SOM quality under intensive rice cropping

During the Green Revolution of the 1960s, plant breeders developed early maturing semi-dwarf varieties of lowland rice that allow two or even three rice crops per year on the same field. Since then, these annual double- and triple-cropped continuous rice systems have become the dominant agricultural land use in the tropical and subtropical lowlands of Asia wherever irrigation water supplies are adequate. This intensive cropping system enabled the Asian rice supply to keep pace with burgeoning populations, as irrigated lowland rice farmers account for about three-quarters of Asia's rice supply (Cassman and Pingali, 1995).

Under intensive cropping, lowland rice soils are submerged for 8–11 months each year. During development of the semi-dwarf varieties in the 1960s, concerns arose over the sustainability of the long-term submerged soil conditions that would accompany continuous cropping. Long-term field experiments were initiated to monitor soil properties under double- and triple-cropped rice. During the subsequent decades, yields gradually declined in some of these long-term experiments (Cassman et al., 1995; Dobermann et al., 2000). For example, in a triple-cropped field trial at the International Rice Research Institute (IRRI) in the Philippines, yields declined during 24 y by 3 ton/ha in the high-yielding dry season and about 2 ton/ha in each of the two wet seasons, or 38% and about 50%, respectively, of the initial yields. There was no evidence for uniform occurrence of pest damage (insects, disease, weeds, nematodes) that would cause this gradual yield decline (Cassman et al., 1995). Phosphorus, K and Zn fertilizers were applied at non-limiting rates, and plant tissue nutrient concentrations excluded any role of boron toxicity. Crop growth characteristics and plant N status suggested that N deficiency during mid- to late-season growth stages contributed to the yield decline. Yet crop response to fertilizer N applications at early crop growth stages had changed little. Based on these trends, Cassman et al. (1995) attributed the yield decline to decreased crop uptake of native soil N, namely soil organic N that becomes available through mineralization of soil organic matter. However, the quantity of soil N in these field experiments had not decreased and in fact had even increased since these experiments were initiated, which focused research efforts on possible changes in the quality of SOM under long-term submerged conditions.

These views were based on the unique nature of N cycling in flooded soil. Inorganic N is not stable in flooded soils for more than a few weeks, as nitrification does not occur and NH_4 is rapidly lost, primarily through NH_3 volatilization when the floodwaters become alkaline. The floodwater pH can increase by as much as two units following urea hydrolysis or photosynthesis by floodwater microorganisms (Keeney and Sahrawat, 1986; Reddy et al., 1990). During the years of declining yields in the long-term field experiments, most fertilizer N (urea) was applied in one or two applications at early season crop growth stages. Given a 90- to 100-day growing season, consequently, crop N uptake at later growth stages was dependent solely on mineralization of soil organic N, and development of a late-season N deficiency suggests an inhibition of soil N mineralization.

In the 1990s, grain yields of the triple-cropped field experiment were restored to their initial levels, in part because of greater solar radiation but also because of more numerous applications of N fertilizer throughout the growing season and at higher overall rates, providing better synchrony between N supply and crop N demand (Cassman et al., 1995; Dobermann et al., 2000). This yield reversal provided further evidence that changes in soil N supply had contributed to the yield decline.

Assuming a physiological efficiency of 50 kg grain/kg N uptake (Yoshida, 1981), the yield loss in the triple-cropped field was equivalent to a decrease in crop uptake of about 60 kg N/ha season. This quantity is a large proportion of the fertilizer rates that tropical rice farmers typically apply each season (generally 90–150 kg/ha), but it is not a significant proportion of total soil N in the plow layer of the triple-cropped field (2000–3000 kg N/ha). The cause of this substantial yield decline may therefore involve solely a portion of the SOM.

A clear change in the chemical nature of SOM that occurs under intensive rice cropping is the accumulation of phenolic compounds (Olk et al., 1996, 1998, 1999, 2000). The dominant types of phenols detected in rice soils (cinnamyl, syringyl and vanillyl) are derived from plant lignin, which comprises the woody tissues of crop roots and straw. More broadly, phenols accumulate in many anaerobic environments, including streams (Malcolm, 1990) and natural wetlands (Katase, 1993). Anaerobic conditions slow decomposition of many organic materials, but lignin and phenols are especially affected (Tate, 1979; Colberg, 1988). Anaerobic bacteria do not have suitable enzymes for rapid degradation of lignin. Their decomposition pathways of aromatic compounds involve slower and less efficient reactions than those of aerobic microorganisms (Evans, 1977). Concurrent with the slowed rate of lignin decomposition under multiple annual cropping of rice, the input rates of lignin are increased because crop residues and roots are returned to the soil two to three